Electronic Supplementary Information for
Hydrophobic Anatase TiO₂–based Thin Films Modified with Al, Cr Derivatives to Reach Reversible Wettability Control

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Electronic Supplementary Information, S1

As we carried out all the experiments under the same conditions, it can be considered that the amount of organic impurities adhered to surfaces during experimental procedures were nearly identical regardless of the surface morphology. However, we observed that surfaces (b)-(d) converted to hydrophobicity whereas surface (e) remained hydrophilicity and that the hydrophobic conversion behaviors differed depending on surface morphologies as shown in SEM images in Fig. 1. Thus, we considered that such differences are originated from the surface morphologies, and the adsorption of impurity does not play important role.

In addition, to clarify the effect of the adsorption of organic impurities on the surface, we carried out experiments using n-hexane as a model organic impurity. It is known that n-hexane is utilized as a model organic compound existed on a TiO₂ surface, e.g., John T. Yates, Jr. et al., J. Phys. Chem. B, 2005, 109, 15454. The anatase surface
prepared from AACA/TiO$_2$ = 1/10 (Fig. 1(c)) was selected. After the surface was irradiated with UV light, converting the surfaces into highly hydrophilic states with a water contact angle of 0°, the surface was stored in the saturated n-hexane vapor at room temperature (R.T.) in the dark using a sealed vessel in which a laboratory dish injected with liquid n-hexane was set. Note that the vapor pressure of n-hexane is ca. 200 mmHg at R.T. and 1 atom. Fig. S1 shows the hydrophobic conversion behavior of the surface stored in the saturated n-hexane vapor at R.T. in the dark. The behaviors stored in an ambient condition at R.T. in the dark and in a dry oven at 80 °C in the dark (corresponding to the Fig. 2(c)) are also shown in Fig. S1. Compared to the dark storage in the ambient condition at R.T., the water contact angles were somewhat larger during the dark storage in the saturated n-hexane vapor at R.T. However, only the small difference was observed. That is, the hydrophobic conversion behaviors did not change so much even though the organic impurities were adhered on the surface. Therefore, we concluded that the effect of organic impurities was possibly ignored even though they were adhered on surfaces during experimental procedures.

Fig. S1  Hydrophobic conversion behaviors with storage in the dark for the anatase thin film prepared from AACA/TiO$_2$ = 1/10, Fig. 1(c), in ambient condition (a), in hexane condition (b) and in a dry oven at 80 °C (c).
Instead of aluminum acetylacetonate (AACA), chromium acetylacetonate (CACA) as a sublimation agent was used in the weight ratios of STS-01 / CACA = 1/22 (b), 1/17 (c), 1/11 (d) and 1/9 (e). The compositions of surfaces (b)-(e) were estimated to be approximately the same, Cr/(Cr+Ti) = 2/13-2/15.

Fig. S2  Surface (upper) and cross sectional (lower) SEM images of TiO₂ underlayer (a), and TiO₂ overlayers prepared from TiO₂/CACA = 1/22 (b), 1/17 (c), 1/11 (d) and 1/9 (e). With increasing TiO₂/CACA ratio, i.e., descending from (b) to (e), pore area decreased due to the sublimation of a smaller amount of CACA. A and S denote anatase and substrate, respectively. Fig. S1 (c) corresponds to Fig. 4(A).
Figure S3 shows the hydrophobic conversion behavior of surfaces (a) - (e) in Figure S2 when stored in the dark in a dry oven. Noted that the surfaces were irradiated with UV light, converting the surfaces into highly hydrophilic states with a CA of 0°, before observing their conversion behavior after storage in the dark. All the rough surfaces (b)-(d) converted to the hydrophobicity without showing the sigmoidal increase.

Fig. S3  Hydrophobic conversion behaviors with storage in the dark at 80 °C of TiO₂ underlayer (a), and TiO₂ overlayers prepared from TiO₂/CACA = 1/22 (b), 1/17 (c), 1/11 (d) and 1/9 (e). Before storage in the dark, all the surfaces were irradiated with UV light, converting them into highly hydrophilic surfaces. The solid line (c) corresponds to that in Fig. 4 (B).